Radiocarbon in dissolved organic carbon of the Atlantic Ocean

Druffel, Ellen R M ; Griffin, Sheila ; Coppola, Alysha I ; Walker, Brett D

Abstract: Marine dissolved organic carbon (DOC) is produced in the surface ocean though its radiocarbon (¹ C) age in the deep ocean is thousands of years old. Here we show that >10% of the DOC in the deep North Atlantic is of post-bomb origin and that the ¹ C age of pre-bomb DOC is >4900 ¹ C yr, 900 ¹ C yr older than previous estimates. We report ¹ C ages of DOC in the deep South Atlantic that are intermediate between values in the North Atlantic and the Southern Ocean. Finally, we conclude that DOC ¹ C ages are older and a portion of deep DOC is more dynamic than previously reported.

DOI: https://doi.org/10.1002/2016GL068746

Originally published at:
Druffel, Ellen R M; Griffin, Sheila; Coppola, Alysha I; Walker, Brett D (2016). Radiocarbon in dissolved organic carbon of the Atlantic Ocean. Geophysical Research Letters, 43(10):5279-5286.
DOI: https://doi.org/10.1002/2016GL068746

Radiocarbon in dissolved organic carbon of the Atlantic Ocean

by

E. R. M. Druffel, S. Griffin, A. I. Coppola, and B. D. Walker

Department of Earth System Science, U. C. Irvine, Irvine, CA 92697–3100

Resubmitted to *Geophysical Research Letters March 2016*

Abstract Marine dissolved organic carbon (DOC) is produced in the surface ocean though its radiocarbon (^{14}C) age in the deep ocean is thousands of yr old. Here we show that ≥10% of the DOC in the deep North Atlantic is of post-bomb origin and that the ^{14}C age of pre-bomb DOC is ≥4900 ^{14}C yr, ~900 ^{14}C yr older than previous estimates [*Druffel et al.*, 1992]. We report ^{14}C ages of DOC in the deep South Atlantic that are intermediate between values in the North Atlantic and the Southern Ocean. Finally, we conclude that DOC ^{14}C ages are older and a portion of deep DOC is more dynamic than previously reported.

1. Introduction

Marine DOC is the largest pool of reduced carbon (C) in the oceans, about equal to the atmospheric CO_2 reservoir. Though most DOC is produced from photosynthetic uptake of modern DIC in the surface ocean, the bulk ^{14}C ages in deep open ocean DOC ranged from 4000 ^{14}C yr in the Sargasso Sea to 6000 ^{14}C yr in the North and South Pacific [*Druffel and Griffin*, 2015; *Druffel et al.*, 1992; *Williams and Druffel*, 1987]. The deep Southern Ocean DOC ^{14}C age (5600 ^{14}C yr) was much closer to that in the deep Pacific, suggesting that the North Atlantic DOC contained bomb ^{14}C, there was a source of old DOC to the Southern Ocean [*Druffel and Bauer*, 2000] or diverse sources of DOC [*Follett et al.*, 2014]. In the ocean margins, there is evidence of inputs of old DOC in the deep northeast Pacific and the mid-Atlantic Bight off the US coast [*Bauer and Druffel*, 1998] and young DOC to the deep subpolar North Pacific [*Tanaka et al.*, 2010]. Terrestrially-derived DOC was found in the deep Arctic Ocean [*Griffith et al.*, 2012].

We find that the DOC $\Delta^{14}C$ in the deep Sargasso Sea in 2012 was lower than it was in 1989, indicating that bomb ^{14}C levels had decreased over a period of two decades. Implications for the C cycle in the ocean include the presence of a labile pool of DOC in deep water.

2. Methods

Water samples were collected from the North and South Atlantic Ocean during the Repeat Hydrography CLIVAR (Climate Variability and Predictability) program. Sampling included surface and subsurface water, northward Antarctic Intermediate Water (AAIW ~700–1200 m, low salinity, high silica) and Upper Circumpolar Deep Water (1000-2000 m), southward North

Atlantic Deep Water (NADW 1500–4000 m, high oxygen, low silica), and Antarctic Bottom Water (within a few hundred meters of the bottom, cold and dense) [*Jenkins et al.*, 2015a; *Reid*, 1989]. A data-constrained ocean circulation model was used to show that in the South Atlantic, Antarctic water penetrates the NADW in volume-weighted averages that vary from 20-40% [*DeVries and Primeau*, 2011].

Radiocarbon in DOC was measured in seawater samples collected from 3 stations along 32°S on the A10 cruise in October 2011, 4 stations along 20°W on the A16N cruise in July/August 2013, and 4 stations along 65°W on the A22 cruise in March/April 2012 (Figure 1 insets, Table S1 in the supporting information). Samples shallower than 400 m were filtered using precombusted GFF (0.7μM) filters, and all samples were collected in 1L Amber Boston Round glass bottles, and frozen at –20°C at an angle to avoid breakage until analysis at U.C. Irvine (UCI). Samples were diluted with 18.2 MΩ Milli–Q water (DOC concentration 0.5–0.9μM), acidified to pH 2 with 85% phosphoric acid, purged with ultra high purity helium gas (UHP 5.0) and UV–oxidized (UVox) [*Beaupré et al.*, 2007; *Druffel et al.*, 2013; *Griffin et al.*, 2010]. Samples for DIC $\Delta^{14}C$ analyses were prepared according to standard methods [*McNichol et al.*, 1994].

The resultant CO_2 from UVox was converted to graphite on iron catalyst for ^{14}C analysis at the Keck Carbon Cycle Accelerator Mass Spectrometry (AMS) Laboratory at UCI [*Southon et al.*, 2004; *Xu et al.*, 2007]. Total uncertainties for individual DOC $\Delta^{14}C$ values of approximately –500‰ are ±4‰ as determined from analyses of numerous duplicate seawater samples and secondary standards [*Druffel et al.*, 2013]. Total uncertainty for DIC $\Delta^{14}C$ values are ±3‰. Total uncertainties for DOC concentrations are ±1.0μM. Stable C isotopes were measured on splits of the CO_2 samples using a Thermo Electron Delta Plus mass spectrometer; total uncertainty of $\delta^{13}C$ values are ±0.2‰.

3. Results

3.1 DOC $\Delta^{14}C$ and $\delta^{13}C$ Values

In the North Atlantic, the surface DOC $\Delta^{14}C$ values ranged from –306‰ at 60°N to –223‰ at 20°N (Fig. 1a,b and Table S2 in the supporting information). Surface values ranged from –279‰ to –259‰ in the South Atlantic (Fig. 1c). Minimum $\Delta^{14}C$ values were reached by ~800–1100m depth (AAIW) in the North (–441‰ to –395‰) (Figure 1a,b) and South (–477‰ to –466‰, Figure 1c) Atlantic. Generally, the DOC $\Delta^{14}C$ values below 1200m in the North Atlantic decreased with depth. Two values from 2569 and 3576m depth in the northeast Atlantic (32°N) were the lowest (–460‰ and –462‰, respectively) and a value (–370‰) from 1313m depth at the farthest north site (60°N) was the highest (Fig. 1b). The average of deep (>1800m) DOC $\Delta^{14}C$ values from the same location (within 145 km) in the Sargasso Sea are 19‰ higher in 1989 (–396±10‰ n=6) than those in 2012 (–415±8‰ n=5) (Fig. 1a).

The DOC $\Delta^{14}C$ values from the South Atlantic below 1200m averaged –471±2se‰ (n=19), and were significantly lower than those in the North Atlantic. Values below 3500 m depth were significantly higher in the southeast basin (–464 ± 4‰ n=3) than those in the southwest basin (–482 ± 3‰ n=3) (Fig. 1c).

Stable C isotope ($\delta^{13}C$) DOC values ranged between –20.5 and –23.0‰, typical of marine produced organic matter (Figure S1 in the supporting information). Values were higher in the deep South Atlantic (–21.3±0.2‰se n=13) and Sargasso Sea (–20.8 ± 0.3‰se n=4) than those in the rest of the deep North Atlantic (–22.3±0.1‰se n=19).

3.2 DOC Concentrations

Concentrations of DOC ranged from 58–76 µM in the upper 40m of the water column (Fig. S2 and Table S2 in the supporting information). Values decreased to about 1000m depth at all stations, and average values in the deep Atlantic were significantly lower in the south (38.1 ± 1.1 µM n=22) than in the north (40.9 ± 1.3 µM n=23) (Figure S2 in the supporting information).

3.3 DIC $\Delta^{14}C$ Values

New DIC $\Delta^{14}C$ values are available for the South Atlantic samples (2011) and 2 depths from the Sargasso Sea station (2012) (Figure 1d). Surface DIC $\Delta^{14}C$ values ranged from +47–54‰ in the South Atlantic and was +58‰ in the Sargasso Sea. Values in the South Atlantic decreased steadily to ~1000m depth and averaged -127‰ below 1200m. Values in the southwest basin were higher at 2400m and 3100m, and lower at 3900 and 4300m, than those in the southeast basin, which did not vary with depth below 2000m.

4. Discussion

We address three major trends in the DOC $\Delta^{14}C$ data. First, values in the deep North Atlantic varied both temporally and spatially, indicating of the presence of bomb ^{14}C. Second, the decrease of pre-bomb DOC $\Delta^{14}C$ values between the deep North and deep South Atlantic are discussed as possible aging of DOC during the southward transport of NADW. Third, we discuss the possible reasons for the dissimilarity of the deep DOC $\Delta^{14}C$ values in the southwest and southeast basins of the Atlantic. Fourth, the global trends of DOC $\Delta^{14}C$ values in the open ocean are presented and discussed.

4.1 Bomb ^{14}C in North Atlantic DOC and Decadal Variability

There was a wide range of DOC $\Delta^{14}C$ values (–462‰ to –370‰) in the deep North Atlantic below 1200m (Figure 1a,b). Values were highest in the northernmost station (60°N) and lowest in the northeast station at 32°N. This pattern is not surprising because NADW forms by surface-to-deep convection in the Labrador and the Nordic Seas, incorporating bomb ^{14}C into DIC of the Deep Western Boundary Current [*Key et al.*, 2004; *Stuiver and Ostlund*, 1980]. It stands to reason that bomb ^{14}C would also be present in DOC in the Sargasso Sea during the 1989 cruise. Notwithstanding, there were six very low DOC $\Delta^{14}C$ values, the three deepest samples from 32°N (–460, –462‰, –452‰) and the deepest sample from 45°N (–453‰) in the northeast Atlantic, and the two deepest samples from 20°N in the Puerto Rican Trench (–452‰, –456‰) in the northwest Atlantic (Figure 1a,b and Table S2 in the supporting information). The DOC concentrations of these 6 samples (average 38.9±2.1µM) are not significantly different from the remaining deep samples at these sites (average 40.5±1.9µM n=9). We hypothesize that the average of the six low $\Delta^{14}C$ values (–456±4‰) represents an upper bound estimate of the pre-bomb DOC $\Delta^{14}C$ in the North Atlantic.This is supported by minimal bomb-produced tritium (δ^3H <0.08 TU) at these deep locations [*Jenkins*, 2007; *Jenkins et al.*, 2015b]. This value is 66‰ lower than the previous estimate for the deep North Atlantic DOC $\Delta^{14}C$ value from samples collected in 1989 (–396‰) [*Druffel et al.*, 1992].

We estimate the fraction of post-bomb DOC in the deep north Atlantic in 2012–2013 using a mass balance calculation. Assuming the source of bomb ^{14}C to the deep water was from solublization of organic particles produced in the surface (DIC in the surface waters during the period 1992-2012 averaged 70‰ (Druffel, unpublished data)), and the deep average DOC $\Delta^{14}C$ value was –415‰ (>1800m, excluding pre-bomb values), there was 89% pre-bomb DOC (-456‰) and 11% post-bomb DOC from organic particles (-415‰ = 0.89 • –456‰ + 0.11 • 70‰). Thus, the input of post-bomb DOC to the deep north Atlantic was > 11% of the standing stock of the deep DOC. A similar calculation for the Sargasso Sea site in 1989, assuming the DIC $\Delta^{14}C$ in the surface waters during the previous two decades was +140‰ [*Druffel*, 1989], reveals that there was $\leq$90% pre-bomb DOC and $\geq$10% post-bomb DOC from organic particles (-396‰ = 0.90 • –456‰ + 0.10 • 140‰).

We observed a temporal shift in DOC $\Delta^{14}C$ values in the deep Sargasso Sea. Here, the average deep value was 19‰ higher in 1989 than in 2012. This decrease was likely not the result of a change in the production of NADW, which has not changed in the last decade [*Fischer et al.*, 2010]. Also, seasonal variability of the deep sea DOC pool is unlikely, because deep ocean DOC $\Delta^{14}C$ time series have not observed temporal changes [*Bauer et al.*, 1998; *Beaupré and Druffel*, 2009]. Input of aged DOC from hydrothermal systems is also not likely the cause of the decrease in deep DOC $\Delta^{14}C$ in the Atlantic given low $\delta^{3}H$ values in these waters (Figure S3 in the supporting information). We hypothesize that the 19‰ higher average DOC $\Delta^{14}C$ value in 1989 represents a higher relative contribution of bomb ^{14}C to the DOC pool than was present in 2012–2013.

To test this hypothesis, we compare the amount of post-bomb DOC in the deep Sargasso Sea in 1989 to net production of organic C exiting the surface ocean. If we assume that a minimum of 10% of the C exported from the mixed layer at the BATS site (32°10′N 64°30′W) was converted to DOC (0.10 • 3±1 mole C m^{-2} yr^{-1} = 0.30 mole C m^{-2} yr^{-1}) [*Emerson*, 2014], then the replacement time of the DOC in a 1 m^2 area of the deep ocean (2500 m^3 • 0.043 mol m^{-3} = 108 mol C) (see Table S2 in the supporting information) would have been 360 yr (108 mol C m^{-2} / 0.30 mole C m^{-2} yr^{-1}). To replace 10% of the DOC in a 1 m^2 area of the deep ocean would have taken about 36 yr (0.10 • 360 yr), which is approximately equal to the time that bomb ^{14}C had been in the ocean from the time of the first sampling of DOC in the Sargasso Sea (1989–1957 = 32 yr). This simple calculation indicates that DOC in the deep Sargasso Sea is likely a heterogeneous mixture that contains distinct $\Delta^{14}C$ signatures with different cycling rates. We determine that $\geq$ 4µM DOC has ages of 10–30 yr (post-bomb) and $\leq$39µM has ages of centuries. This has important implications for the role of DOC in the oceanic C cycle of the Atlantic (see Section 5).

Evidence that deep DOC is a heterogeneous, isotopic mixture in the surface ocean is shown by a Keeling plot (Figure S4 in the supporting information), which identifies the $\Delta^{14}C$ value of an excess component added to a background pool [*Mortazavi and Chanton*, 2004]. Keeling plots of DOC concentration^{-1} versus DOC $\Delta^{14}C$ value were linear, and suggested rapid export out of the upper 85m, and advection between 100–1000m [*Beaupré and Aluwihare*, 2010]. Keeling plots of the Atlantic data reveal y-intercepts that were similar to the DIC $\Delta^{14}C$ of the surface waters at each site (Table S3 in the supporting information), indicating that the excess DOC originated from recent production in the surface ocean. Similar results were obtained from Keeling plots of

South Pacific data [*Druffel and Griffin*, 2015] (Figure S4 and Table S3 in the supporting information).

Additionally, DOC $\delta^{13}C$ values in the North Atlantic (1989–2013) were generally lower than those in the South Atlantic (Figure S1 of the supporting information), which may indicate that there is a larger ^{13}C Suess Effect (presence of mostly fossil fuel-derived CO_2) in the deep North Atlantic than that in the South Atlantic. This would support the premise that bomb ^{14}C was present in the North Atlantic, however it is also possible that input of fossil carbon may have contributed to a decrease in DOC $\Delta^{14}C$ values in the North Atlantic.

4.2 Aging of DOC in North Atlantic Deep Water

Our estimate of the upper bound for the pre-bomb DOC $\Delta^{14}C$ value in the deep North Atlantic (–456±4‰ section 3.3.1) corresponds to a ^{14}C age of 4900±60 ^{14}C yr. This means that the pre-bomb ^{14}C ages of the deep basins of the North Atlantic and North Pacific have decreased from 4000 ^{14}C and 6000 ^{14}C yr, to 4900 and 6000 ^{14}C yr.

The difference between the pre-bomb ^{14}C ages of the North (4900±60 ^{14}C yr) and South (5120±35 ^{14}C yr) Atlantic DOC is 220±95 ^{14}C yr. This difference is equal to the estimated replacement time (250 ^{14}C yr) determined from the deep DIC ^{14}C ages in the Atlantic [*Stuiver et al.*, 1983]. However, this may be fortuitous due to the presence of bomb (and possibly pre-bomb) DOC from the dissolution of surface particles [*Smith et al.*, 1992a] in the deep waters. This similarity may indicate that DOC has been transported with NADW as it traveled southward, but we cannot demonstrate this because DOC is not an isolated pool.

4.3 Spatial Variability of $\Delta^{14}C$ in the Deep South Atlantic

Comparison of the DOC and DIC $\Delta^{14}C$ values from the South Atlantic in 2011 reveals that both were high in the upper 1000 m indicating presence of bomb ^{14}C (Figure 1c,d). Bomb ^{14}C penetration was several hundred meters deeper in the DIC pool. In the two deepest samples (3900 and 4300 m), the DIC $\Delta^{14}C$ values in the southwest basin were 9‰ and 22‰ lower than those in the southeast basin (Fig. 1d). Older waters in the west suggest that they may be less well-ventilated than those in the east. The DOC $\Delta^{14}C$ values from the west were also lower (by 11-24‰) in the deepest three samples (3500–4300m) than those in the east (Fig. 1c).

Higher $\Delta^{14}C$ values of DIC and DOC in the deep southeast basin could be the result of dissolution of high $\Delta^{14}C$ particulate organic carbon (POC) from the surface, or mixing of Southern Ocean waters into the deep South Atlantic. The amount of surface POC (pre-bomb $\Delta^{14}C$ value of –70‰ [*Druffel*, 1996]) required to increase the deep DOC $\Delta^{14}C$ value from –483‰ (west basin average) to –463‰ (east basin average) is 5% of the DOC pool. This value would be 4% if the surface POC $\Delta^{14}C$ value contained bomb ^{14}C (+70‰). We note that net primary production is higher in the southeast Atlantic than that in the southwest Atlantic [*Falkowski*, 2014], which would cause a higher input of surface-derived POC to the deep southeast basin, and provide a mechanism for the higher DOC $\Delta^{14}C$ values. Second, DeVries and Primeau (2011) used a data-constrained ocean circulation model to characterize the distribution of water masses and their ages in the global ocean and showed that the ratio of Southern Ocean to NADW at 32°S in the South Atlantic was about 1:3. There was no evidence that this ratio was different in the southeast and southwest basins (F. Primeau, personal communication). Thus, we are not able to determine if dissolution of POC to DOC or physical mixing is the reason for the DIC and DOC $\Delta^{14}C$ offsets we observe between the southwest and southeast basins of the Atlantic.

4.4 Global Trends of DOC $\Delta^{14}C$ Values

There are seventeen DOC $\Delta^{14}C$ profiles available for the Pacific and Atlantic Ocean basins, including the nine new profiles presented here. Though the number of profiles is limited, they improve our understanding of the global ocean $DO^{14}C$ cycle. To portray the global DOC $\Delta^{14}C$ trends better, a 3-dimensional animation is presented that displays the $\Delta^{14}C$ profiles in these basins [*Schlitzer*, 2015] (DOC 14C animation). The animation shows the gradual decrease of DOC $\Delta^{14}C$ values in the deep water, from high values in the far North Atlantic (–410‰ green) to lower values in the South Atlantic (–470‰ aqua). There are areas of low $\Delta^{14}C$ values (–456‰ turquoise) in the northwest at 20°N and the northeast Atlantic, portraying the water masses we hypothesize as pre-bomb DOC in these slower ventilated regions.

The $\Delta^{14}C$ values decreased further at the Southern Ocean site (–500‰ blue), and fell to an even lower value (–525‰ purple) in the South and North Pacific basins. As noted above, the surprising lack of a gradient in $\Delta^{14}C$ values in the Pacific basin indicates that processes other than ^{14}C decay during northward transport are at work [*Druffel and Griffin*, 2015]. Values were lowest (–550‰ fuchsia) off California in the northeast Pacific, and were believed to have been influenced by sources of old C from the continental margin [*Bauer and Druffel*, 1998]. The surface waters at all locations were similar (average –255±35‰ n=18), with the exception of the

Southern Ocean (–372±5‰ n=3) where surface-to-deep mixing bring lower $\Delta^{14}C$ water to the surface.

The gradual decrease of deep DOC $\Delta^{14}C$ values from the North Atlantic to the South Atlantic suggests that most of the DOC ages as it is transported southward in NADW. This aging is portrayed in Figure 3, which shows DOC concentrations versus ^{14}C ages for each sitein the Atlantic, SOce and the Pacific (>1500m). The decrease in DOC concentration and ^{14}C ages from the North Atlantic to the Pacific mimics the flow of NADW along the deep ocean conveyor, and is lowest for both quantities in the Pacific basin. This general decrease agrees with previous studies of global deep DOC concentrations along the deep ocean conveyor [*Hansell et al.*, 2012]. The SOce values lie off of this relationship suggesting an additional source of DOC [*Druffel and Bauer*, 2000] or different isotopic signatures within deep DOC [*Follett et al.*, 2014].

An estimate of the transport time of most of the DOC from the northern North Atlantic to the Southern Ocean, assuming decay of ^{14}C in DOC is the major cause of the gradient, is approximately 670 ^{14}C yr (5570 minus 4900 ^{14}C yr). The transport time of DOC from the Southern Ocean to the Pacific basin is approximately 400 ^{14}C yr (5970 minus 5570 ^{14}C yr). Thus, the total time of transport of deep DOC from the northern North Atlantic to the Pacific basin is approximately 1080 ^{14}C yr. This value is similar to the sum of the deep water replacement times for DIC in the Atlantic and the Pacific (250 + 510 = 760 yr) [*Stuiver et al.*, 1983]. These estimates do not account for the change of DIC and DOC in the deep water by particle dissolution and remineralization, which would make the transport time estimates too low. They also ignore preferential remineralization of DOC that has different $\Delta^{14}C$ values from the bulk value. As one would expect younger (higher $\Delta^{14}C$), more labile DOC to be remineralized preferentially, this would cause the transport time estimates determined above to be too high.

5. Implications for the DOC Cycle in the Ocean

Though the bulk DOC ages in the deep sea are thousands of ^{14}C yr old, we show that a portion of this DOC is post-bomb, and that the $\Delta^{14}C$ values in the deep Sargasso Sea have changed on decadal time scales. We estimate that the pre-bomb age of DOC in the North Atlantic (4900 ^{14}C yr) is older than previously reported (4000 ^{14}C yr [*Druffel et al.*, 1992]). These results change our current understanding of labile vs. refractory DOC in the deep ocean.

Whereas $\geq$10% of the DOC in the deep North Atlantic is of post-bomb origin, $\leq$90% of the DOC has an older ^{14}C age of 4900 ^{14}C yr. There is a fraction of the pre-bomb DOC that has ^{14}C ages much greater than the timescale of meridional overturning circulation. Ancient DOC has been identified in ultrafiltered DOC as black C with ages of 18000 to 21800 ^{14}C yr [*Ziolkowski and Druffel*, 2010]. Whether this ancient DOC was put into the ocean pre-aged (e.g. hydrothermal sources), or had aged by decay within the deep sea, is an open question.

Though the ^{14}C age of pre-bomb DOC in the North Atlantic was ~4900 ^{14}C yr, the turnover time of DOC was much shorter. This is because ^{14}C age and turnover time (1/k, where $k=\Sigma(1/^{14}C$ age)) are equal only for a homogeneous C pool. For DOC composed of two pools with different ^{14}C ages (e.g. 30 and 4900 ^{14}C yr), the turnover time (284 yr = 1/(0.1/30 + 0.9/4900)) is much less than its ^{14}C age due to dominance of the quickly cycled DOC term [*Loh et al.*, 2004; *Trumbore and Druffel*, 1995].

The differences between the Atlantic DOC $\Delta^{14}C$ profiles presented here reveal that the DOC cycle is far more dynamic, both spatially and temporally, than previously believed, particularly in the North Atlantic. DOC $\Delta^{14}C$ values for samples collected from the SOce in 1995 [*Druffel and Bauer*, 2000] have a lower average value (–500 ± 12‰) below 1500m depth than those in the North or South Atlantic, and are more variable. This suggests that more SOce measurements are needed to constrain the cycling of DOC in the global ocean. We note that the biogeochemical cycling of DOC is more clearly resolved when isotopic measurements are included vs. concentration measurements alone. A more complete global picture of DOC cycling will be further illuminated with future $\Delta^{14}C$ and compound specific $\Delta^{14}C$ measurements.

Acknowledgements

The authors gratefully acknowledge the technical assistance of Danielle Glynn and Christopher Glynn, the advice and support of John Southon, the support of chief scientists Alison MacDonald, Ruth Curry, and Molly Baringer, the guidance of Jim Swift, and the field support of the crews of the R/V Atlantic and the NOAAS Ronald H. Brown. We thank Francois Primeau for his advice on deep ocean mixing. We thank Reiner Schlitzer for the 3D animation of DOC $\Delta^{14}C$ values (Alfred Wegener Institute, Helmholtz Centre for Polar and Marine Research, Bremerhaven). This work was supported by the NSF Chemical Oceanography Program (OCE–0961980 and OCE–141458941), the Kavli Foundation, the Keck Carbon Cycle AMS Laboratory,

and the NSF/NOAA–funded U.S. Repeat Hydrography Program. The data supporting the conclusions can be obtained in the supporting information, and at the Repeat Hydrography Data Center at the CCHDO website http://cdiac.ornl.gov/oceans/RepeatSections/clivar.html.

References

Bauer, J., and E. Druffel (1998), Ocean margins as a significant source of organic matter to the deep open ocean, *Nature*, *392*, 482-485.

Bauer, J., E. Druffel, P. Williams, D. Wolgast, and S. Griffin (1998), Inter– and intra–annual variability in isotopic (14C and 13C) signatures of dissolved organic carbon in the eastern North Pacific Ocean, *Journal of Geophysical Research*, *103*, 2867-2882.

Beaupré, S., and E. Druffel (2009), Constraining the propagation of bomb-radiocarbon through the dissolved organic carbon (DOC) pool in the northeast Pacific Ocean, *Deep-Sea Research I*, *56*, 1717-1726.

Beaupré, S., and L. Aluwihare (2010), Constraining the 2-component model of marine dissolved organic radiocarbon, *Deep Sea Research II*, *57*, 1493-1503.

Beaupré, S., E. Druffel, and S. Griffin (2007), A low-blank photochemical extraction system for concentration and isotopic analyses of marine dissolved organic carbon, *Limnology and Oceanography Methods*, *5*, 174-184.

DeVries, T., and F. Primeau (2011), Dynamically and observationally constrained estimates of water-mass distributions and ages in the global ocean, *Journal of Physical Oceanography*, *41*, 2381-2401.

Druffel, E. (1989), Decade time scale variability of ventilation in the North Atlantic determined from high precision measurements of bomb radiocarbon in banded corals, *Journal of Geophysical Research*, *94*, 3271-3285.

Druffel, E. (1996), Post-bomb radiocarbon records of surface corals from the tropical Atlantic ocean, *Radiocarbon*, *38*(3), 563-572.

Druffel, E., and J. Bauer (2000), Radiocarbon distributions in Southern Ocean dissolved and particulate organic carbon, *Geophysical Research Letters*, *27*, 1495-1498.

Druffel, E., and S. Griffin (2015), Radiocarbon in dissolved organic carbon of the South Pacific Ocean, *Geophys. Res. Lett.*, *42*, 4096-4101.

Druffel, E., P. Williams, J. Bauer, and J. Ertel (1992), Cycling of dissolved and particulate organic matter in the open ocean, *Journal of Geophysical Research*, *97*, 15639-15659.

Druffel, E., J. Bauer, S. Griffin, S. Beaupré, and J. Hwang (2008), Dissolved inorganic radiocarbon in the North Pacific Ocean and Sargasso Sea, *Deep-Sea Research*, *55*(4), 451-459.

Druffel, E., S. Griffin, B. Walker, A. Coppola, and D. Glynn (2013), Total uncertainty of radiocarbon measurements of marine dissolved organic carbon and methodological recommendations, *Radiocarbon*, *55*(2-3), 1135-1141.

Emerson, S. (2014), Annual net community production and the biological carbon flux in the ocean, *Global Biogeochemical Cycles*, *28*, 14-28.

Falkowski, P. (2014), The biogeochemistry of primary production in the sea, *Treatise on Geochemistry (Second Edition)*, *10: Biogeochemistry*, 163-187.

Fischer, J., M. Visbeck, R. Zantopp, and N. Nunes (2010), Interannual to decadal variability of outflow from the Labrador Sea, *Geophys. Res. Lett.*, *37*, doi:10.1029/2010GL045321.

Follett, C., D. Repeta, D. Rothman, L. Xu, and C. Santinelli (2014), Hidden cycle of dissolved organic carbon in the deep ocean, *Proceedings of the National Academy of Sciences*, *111*(47), 16706-16711.

Griffin, S., S. Beaupré, and E. Druffel (2010), An alternate method of diluting dissolved organic carbon seawater samples for 14C analysis, *Radiocarbon*, *52*(2), 1224-1229.

Griffith, D., A. McNichol, L. Xu, F. McLaughlin, R. MacDonald, K. Brown, and T. Eglinton (2012), Carbon dynamics in the western Arctic Ocean: insights from full-depth carbon isotope profiles of DIC, DOC, and POC, *Biogeosciences*, *9*, 1217-1224.

Hansell, D. (CA Carlson), 2001, *Deep-Sea Research II*, *48*, 1649-1667.

Hansell, D., C. Carlson, and R. Schlitzer (2012), Net removal of major marine dissolved organic carbon fractions in the subsurface ocean, *Global Biogeochemical cycles*, *26*, doi:10.1029/2011GB004069.

Jenkins, W. (2007), Tritium and helium-3 data from A22 cruise in 2003, edited by CChdo.ucsd.edu/cruise, CCHDO.

Jenkins, W., S. S. Jr., E. Boyle, and G. Cutter (2015a), Water mass analysis for the U.S. GEOTRACES (GA03) North Atlantic sections, *Deep Sea Research II*, *116*, 6-20.

Jenkins, W., D. L. III, B. Longworth, J. Curtice, and K. Cahill (2015b), The distributions of helium isotopes and tritium along the U.S. GEOTRACES North Atlantic sections (GEOTRACESGAO3), *Deep Sea Research II*, *116*, 21-28.

Key, R., A. Kozyr, C. Sabine, K. Lee, R. Wanninkhof, J. Bullister, R. Feely, F. Millero, C. Mordy, and T.-H. Peng (2004), A global ocean carbon climatology: Results from Global Data Analysis Project (GLODAP), *Global Biogeochemical Cycles*, *18*, doi:10.1029/2004GB002247.

Loh, A. N., J. E. Bauer, and E. R. M. Druffel (2004), Variable aging and storage of dissolved organic components in the open ocean, *Nature*, *430*, 877-881.

McNichol, A. P., G. Jones, D. Hutton, and A. Gagnon (1994), The rapid preparation of seawater TCO2 for radiocarbon analysis at the National Ocean Sciences AMS Facility, *Radiocarbon*, *36*(2), 237-246.

Mortazavi, B., and J. Chanton (2004), Use of Keeling plots to determine sources of dissolved organic carbon in nearshore and open ocean systems, *Limnology and Oceanography*, *49*(1), 102-108.

Reid, J. (1989), On the total geostrophic circulation of the South Atlantic Ocean: Flow patterns, tracers and transports, *Progress in Oceanography*, *23*, 149-244.

Schlitzer, R. (2015), 3D Scene of DOC Δ14C in the World Ocean, edited, Alfred Wegener Institute, Helmholtz Centre for Polar and Marine Research, **Bremerhaven**.

Smith, D., M. Simon, A. Alldredge, and F. Azam (1992a), Intense hydrolytic enzyme activity on marine aggregates and implications for rapid particle dissolution, *Nature*, *359*, 139-142.

Smith, D., M. Simon, A. Alldredge, F. A. I. hydrolytic, and e. a. o. m. a. a. i. f. r. p. dissolution (1992b), Intense hydrolytic enzyme activity on marine aggregates and implications for rapid particle dissolution, *Nature*, *359*(6391), 139-142.

Southon, J. R., M. Santos, K. C. Druffel-Rodriguez, E. R. M. Druffel, S. E. Trumbore, S. G. X. Xu, S. Ali, and M. Mazon (2004), The Keck Carbon Cycle AMS Laboratory, U.C.I.: Initial operation and a background surprise, *Radiocarbon*, *46*(1), 41-50.

Stuiver, M., and H. G. Ostlund (1980), GEOSECS Atlantic radiocarbon, *Radiocarbon*, *22*, 1-24.

Stuiver, M., P. D. Quay, and H. G. Ostlund (1983), Abyssal water 14C distribution and the age of the world oceans, *Science*, *219*, 849-851.

Tanaka, T., S. Otosaka, M. Wakita, H. Amano, and O. Togawa (2010), Preliminary result of dissolved organic radiocarbon in the western North Pacific Ocean, *Nuclear Instruments and Methods in Physics Research B*, *268*, 1219-1221.

Trumbore, S. E., and E. R. M. Druffel (1995), Carbon isotopes for characterizing sources and turnover of non-living organic matter, in *Role of Nonliving Organic Matter in the Earth's Carbon Cycle*, edited by R. Z. a. C. Sonntag, pp. 7-22, John Wiley & Sons, New York.

Williams, P. M., and E. R. M. Druffel (1987), Radiocarbon in dissolved organic carbon in the central North Pacific Ocean, *Nature*, *330*, 246-248.

Xu, X., S. Trumbore, S. Zheng, J. Southon, K. McDuffee, M. Luttgen, and J. Liu (2007), Modifying a sealed tube zinc reduction method for preparation of AMS graphite targets: Reducing background and attaining high precision, *Nuclear Instruments and Methods in Physics Research B*, *259*, 320-329.

Ziolkowski, L., and E. Druffel (2010), Aged black carbon identified in marine dissolved organic carbon, *Geophysical Research Letters*, *37*, 10.1029/2010GL043963.

Figure 1. DOC Δ^{14}C values in samples collected from a) the northwest Atlantic along ~65°N (A22 cruise 2012), b) the northeast Atlantic along ~20°W (A16N cruise 2013), and c) the South Atlantic along 32°S (A10 cruise 2011). d) DIC Δ^{14}C values in samples collected from the South Atlantic along 32°S (A10 cruise 2011) and the SS (A22 cruise in 2012 large red diamonds). DOC and DIC Δ^{14}C values from the SS (in 1989 [*Druffel et al.*, 1992] red dashed line are shown for comparison.

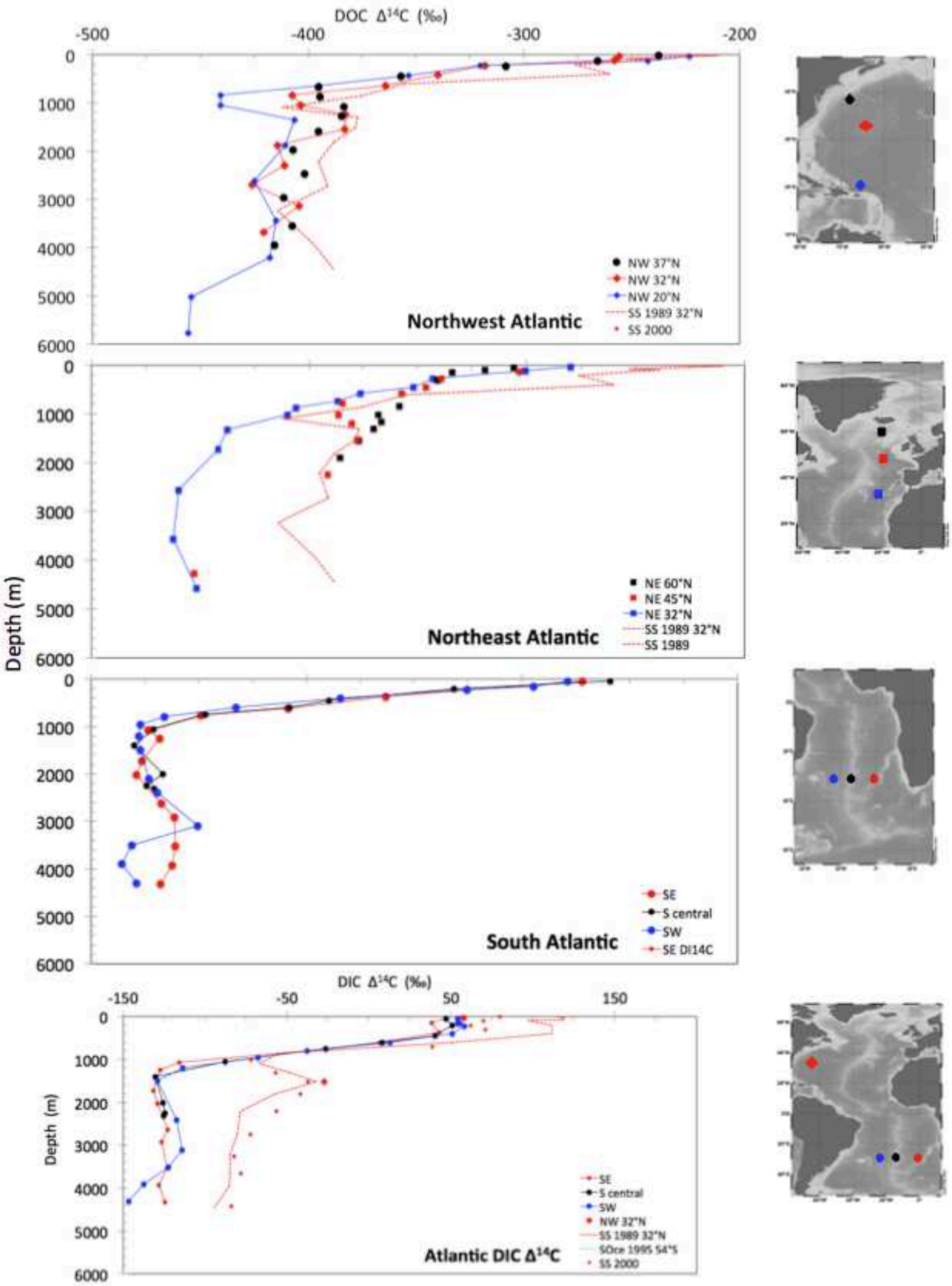

Figure 2. DOC 14C animation Three-dimensional animation produced by Reiner Schlitzer using Ocean Data View software.

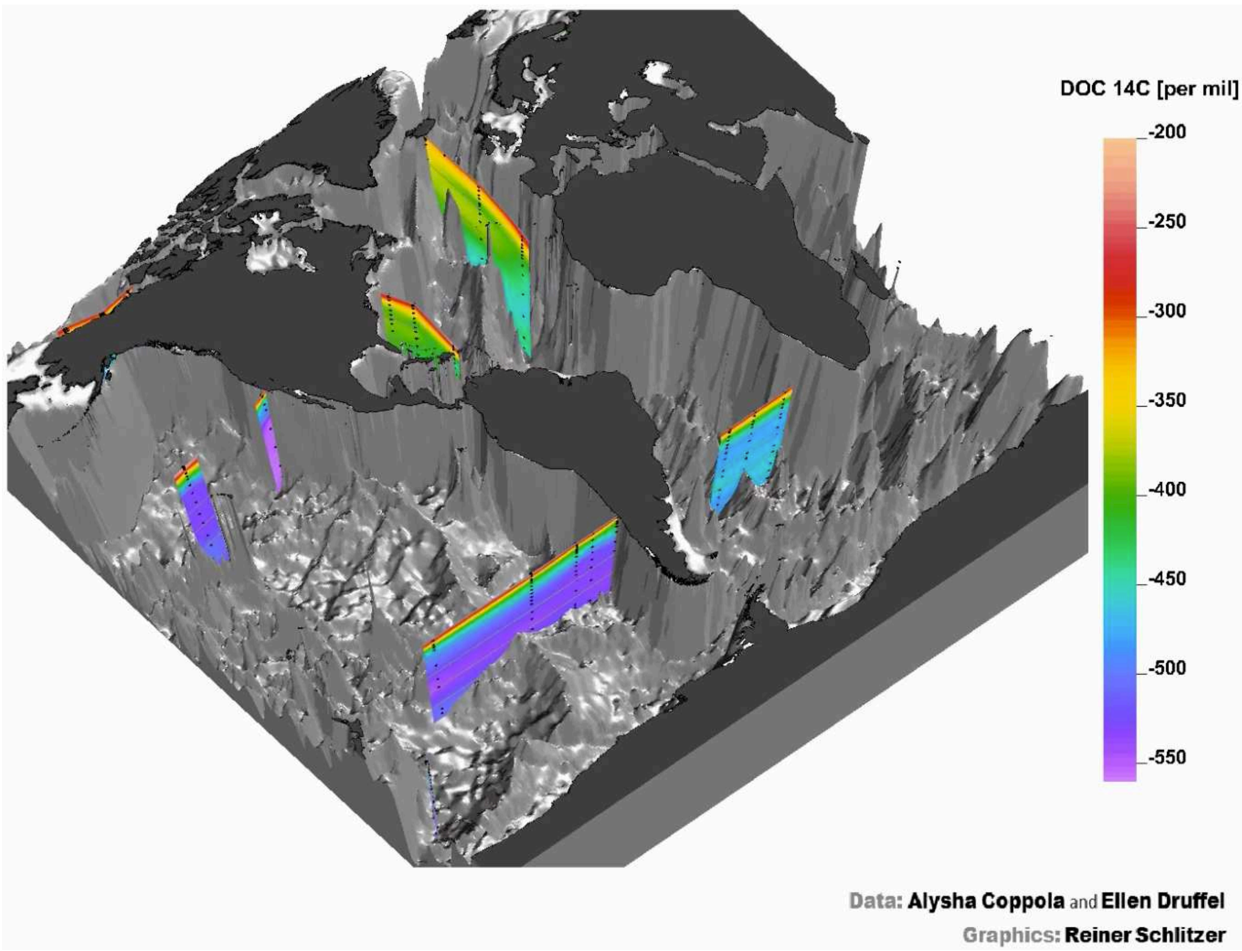

Figure 3. DOC concentrations vs. DOC ^{14}C ages for samples >1500m depth. Data are from the Atlantic (this work), SS and north central Pacific [*Druffel et al.*, 1992], SOce ([*Druffel and Bauer*, 2000], and South Pacific [*Druffel and Griffin*, 2015]. Solid line is the Model II geometric mean regression of all points (except SOce), and dashed lines are the confidence limits (upper and lower 95%) that an individual point will fall on this line.